Decolourization of Waste Water From Bleached-Kraft Pulp & Paper Mill Using Alum and Clay

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SUMMARY

Bleaching operation, in a bleached kraft mill with black liquor recovery furnace is the major source of coloured waste water. Since the colouring substance is bio-refractory, decolourization of such a waste can not be brought about by conventional biological treatment. Of the various treatment methods suggested, lime treatment is the only method which has actualty been used. This particular treatment however, yields effluent of high pH, which is then further treated before conventional treatment. Therefore the approach incorporated in the present investigation, aims at improving alum coagulation by adding clay. Clay assisted alum coagulation has been shown to yield flocs which settle faster and forms a more compact sludge. The work embodied in the present project also incorporates the continuous treatment of coloured waste water in a sludge blanket clarifier. (Lab. Model). The performance of the model has been evaluated with reference to alum coagulation and alum alongwith two different doses (500 and 800 mg/l) of clay.

INTRODUCTION

Colour removal from waste streams is a difficult problem confronting the pulp and paper industry. Effluent from bleaching process are highly coloured and of significant volume : typically 75,000 litres metric ton of pulp. The decolourization and detoxification of bleachary effluents have become serious problems of the industry in anticipation of increasingly stringent regulations specifying allowable toxicity levels and further regulation of colour level of the pulp mill effluents. Out of the total discharge of colour, more than 90% originates from bleach plant effluent.

Pulp bleaching is necessary to brighten the pulp and the bleaching operation sequence depends on the type of pulp bleached and the end product produced. The bleaching process. essentially is a delignification reaction. For chemical pulps viz. kraft, sulfite and neutral sulfite pulps, initial removal of lignin is achieved by cooking with alkalies, sulfides or sulfites. It is then followed by oxidative multistage bleaching using bleaching agents like chlorine (C) chlorine dioxide (D), hypochlorite (H) etc. and caustic extraction (E). The degree of brighteness obtained is of course directly related to the degree of lignin removal obtained prior to oxidative bleaching. The application of any of the bleaching agent is always followed by alkali extraction (E) After each stage in multistage bleaching, a washing cycle is necessary. Therefore, water reuse is vital since 3-5 stage bleaching operation are quite common. Greater brightness can be achieved if smaller amounts of bleaching agents are applied in successive stages with washing between each stage, the resultant increase in water usage (as well as capital cost and fibre loss) is a limiting factor. With the development of chlorine dioxide as a bleaching agent, many modern bleach plant use only five stages to produce white and strong plup. Bleaching operation is the major source of waste water from the kraft pulp and paper mill, is with black liquor recovery furnace. The combined effluent from the bleaching section of a pulp and

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paper mill is highly coloured [1,2]. In bleached kraft mills. 60-70% of the total colour is typically derived from one effluent stream, the first caustic extract after chlorinarion. The colouring body in the waste is organic in nature and is comprised of wood extractives, lignin and its degradation products formed by the action of chiorine or chlorine dioxide on lignin [3]. Lignin in the waste is present both as hydrophilically dispersed, coloured high molecular wt. fractions as well as low molecular wt. colourless soluble fraction. The later one is amenable to oxidation and former fraction is easily coagulated and flocculated and precipitated [4].

The colour removal problem is made worse by the fact that lignin compounds responsible for colour are biologically refractive. Thus, biological i e. secondary, treatment processes are not effective in removing colour. No doubt, the colour of effluent is a problem for which effective technical solutions now exist. The recent approach in this area to develop the concept of installing non-polluting, closed cycle effluent free bleach plant [5,7]. The first venture to build an effluent free and kraft mill was launched by Great Lakes Paper Co. Canada [5]. The mill incorporated an $ 8 million, closed cycle process into the standard kraft mill flow sheet. It has achieved pollution free mill by recycling bleach plant effluent through the standard black liquor recovery cycle and from the resulting white liquor separating out the salt (Nacl), which becomes the basic raw material for the manufacture of chlorine dioxide [6,7]. The significant features of the process are :

a) a tight counter current washing in the bleach plant to reduce the volume of the waste.

b) effluent from the extraction stage is decolourized using sorption resin and used as wash water in the chlorination stage.

Under the present set of conditions such alterations are not economically viable in developing countries. A variety of other methods for removing colour from caustic extract effluent have been fairly effective in some situations. These include absorption by activated charcoal [8] or synthetic resins [6,9]. ion exchange [10], reverse osmosis [11,12], chemical or photochemical oxidation [13-16], electrolytic coagulation [17,18], phase separation using long chain aliphatic amines emulsified in hydrocarbon soluents [11,19,20], precipitation using polyamines [21], alum [22-23], ferric salts [24], magnesium salts [25] and massive lime doses [26]. The cost of these techniques is still fairly high and this restricts their use to specific local situations. The massive lime treatment as well as modified lime treatment of bleachery waste have been put to actual practice [27,28]. The method however, has certain limitations viz. high pH, and residual lemonade colour of the treated effluent, massive lime requirement [29] etc. Therefore, still good deal of research is going on in this field to develop alternative methods. In view of. this, an attempt is also being made in this laboratory to develop an economically and technically feasible treatment process to remove colour and toxic substances from the bleachery waste.

As regards this, it has already been established by jar tests that alum-clay coagulation of colouring material in the waste water is more workable than the reported alum [30]. Moreover, upflow clarifier units should be given serious consideration in those processes where reactions can be made to proceed more effectively at higher solid concentration or at greater solid retention times than can be obtained in flow through units [31]. Therefore, in the present project, an attempt has been made to continuously treat coloured waste water from a bleached kraft mill in an upflow clarifier unit. The larger particles in the clariflocculator, accumulate to form a suspended layer, or sludge blanket, which agglomerates incoming small suspended particles.

MATERIALS AND METHODS

The total waste water from a bleached kraft pulp and paper mill was used for experimentation. Single lot of waste water was stored in underground cement concrete tanks and the waste characteristics were regularly monitored. Commercial alum marketed by Delhi cloth and General Mills (DCM) and locally available kalonite clay were used as coagulant in this study. Firstly, jar tests were conducted to determine optimum alum dose and optinum clay dose along with alum. Sludge volume concentration and sludge volume indices of various sludges formed in jars were determined using standard 1 litre graduated cylinders. Colour of the waste water and treated effluent was measured in accordance with the procedure laid down by Carpenter and Berger[32].

The continuous operation of colour removal was studied in a 54 litres capacity upflow clariflocculator of sludge blanket filteration type (suspended solids contact clarifier). The model was designed and fabricated in perspex, based on procedure given by Fair et al [33]. Details of the upflow clarifier and the flow diagram of the set up is indicated in Fig. 1 and Fig. 2. Prior to the entry into the clarifier waste was mixed with alum and clay solutions in calculated amounts in a flash mixer run at about 200 RPM. A two percent solution of alum in water, and two percent suspension of clay in waste water were used for dosing. The dosages were controlled accurately by means of a constant head tank.

In order to evaluate the performance of the clariflocculator, a few parameters, viz. sludge blanket stability, colour removal, COD reduction, escape of suspended solids over the outlet weir were taken into consideration. The waste was admitted to the clariflocculator at different flow rates ranging from 0.65 to 2.7 LPM equivalent surface loading rates being 7300-300,00 litres/sq. metre/day. Flow rates upto 4 LPM were tried. Initially the clariflocculator was run at a slower rate, which enabled the formation of sludge blanket. The sludge blanket thus formed, was able to trap the flocs coming at higher rate. Clariflocculator was run until flocs started escaping heavily over the outlet weir with the treated effluent i. e. until sludge blanket was at highest possible level. Samples were collected at the treated effluent outlet for each flow rate and analysed for various parameters [34]. Flocculator was run using separately alum as a coagulant and to different day doses alongwith optimum alum dose.

RESULTS AND DISCUSSION

The waste water from bleached kraft pulp and paper mill was first characterized. Table I records the characteristics of the untreated as well as treated waste. Initial colour of the waste was 3500 units on Pt, Co. scale. Optimum alum and clay requirements were determined by jar test. Maximum percentage of colour removal (94—95% was taken as a criterion to fix 500 mg/l of alum as an optimum dose. Addition of clay does not in anyway take part in colour removal by alum. Compaction or pelleting of the flocs and sludge takes place by mixing clay to the waste water alum mixture. Clay acts like a weighting agent for the lightflocs. Therefore, optimum clay dose was fixed on the basis of the minimum sludge volme concentration and sludge volume index. By such criteria, the optimum clay does for this waste was 500 mg/l The clay addition was necessitated by the fact that sludge volume concentration (SVC_{30}) was reduced from 20-25% (with alum alone) to 8-10% and sludge volume index (SVI_{30}) φ was lowered from 475 (with alum alone) to 120. Based on these results, the colour of the waste was continuously removed in a clariflocculator using alum with and without clay. Two different doses of clay were used, optimum dose of 500 mg/l and 800 mg/l. Clay doses higher than 800 mg/l did not further improve the sludge settling quality. On the contrary, excess of clay, instead of partcipating in flocculation or pelleting, got seperated and settled discretely.

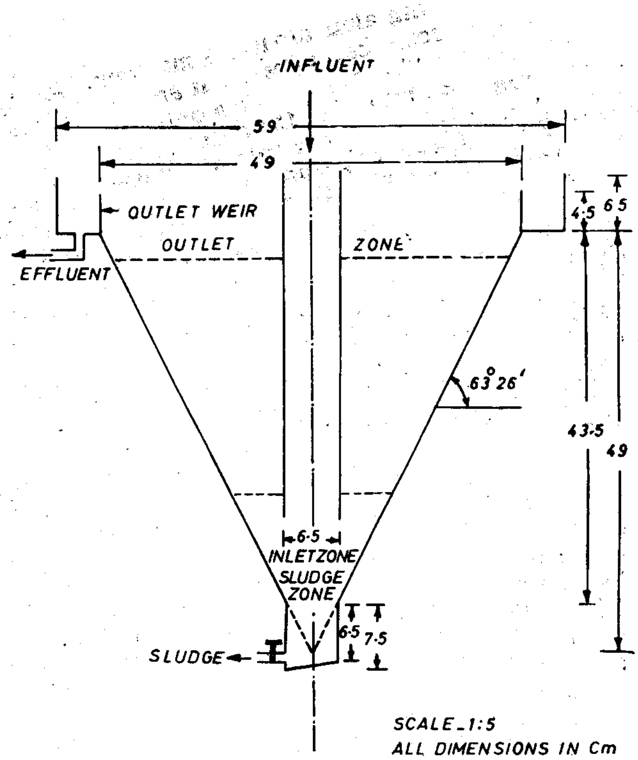

FIG.1_UPFLOW CLARIFLOCCULATOR (SLUDGE BLANKET CLARIFIER)

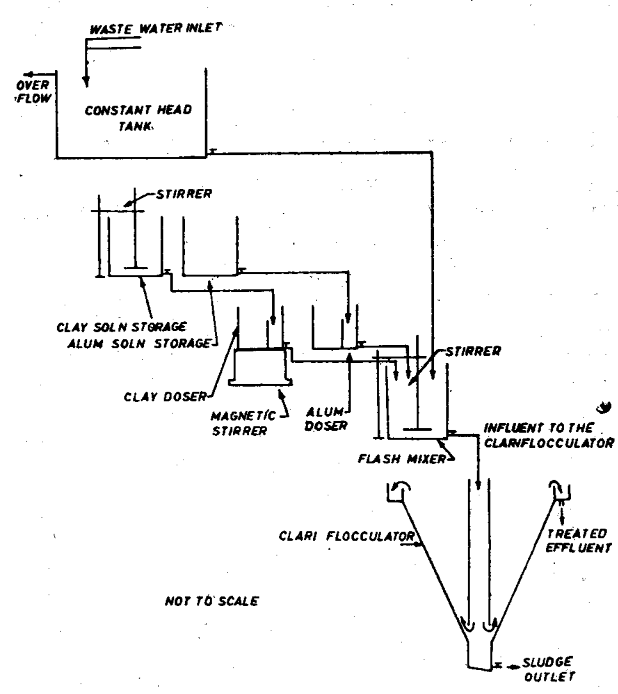

FIG.2. FLOW SHEET OF EXPERIMENTAL SET UP

In an upflow clarifier, the quality of the treated effluents depends on the nature and size of the initially formed sludge blanket. The quality of the sludge blanket depends on the initial characteristics of the influent mixture (i. e. with or without clay) as well as the flow rate at which influent is admitted into the clarifier.

SLUDGE BLANKET

In the case of only alum (no clay), the blanket formed was unstable, light in weight and large in volume. When the flow rate was increased, particularly beyond ILPM (equivalent rise rate 11,300 $1/m^2$/day), the blanket broke up and tended to float upwards forming clouds of sludge. In the laboratory model, blanket could be kept to a maximum level of 25 cm below the crest of the outlet weir at ILPM flow rate. Beyond this level, large amounts of flocs started escaping with the treated effluent. It necessitated frequent desludging.

The sludge, blanket from alum and clay was stable right from the initial stages of the operation. It never tended to float or break even when flow rate was raised to 2.7 LPM (equivalent to 30,000 $1/m^2$/day) and above. The studies, however, were limited to this level as flow rates above this resulted in poor removal of COD. The colour removal remained more or less the same at different flow rates. Flocculator could be operated in this case with sludge blanket very near (about 2 cm below the crest level) to the crest level of the outlet weir, maintaining a very small escape of SS. The clariflocculator was continuously operated for four to five hours at a flow rate of 2.7 LPM without interrupting for desludging.

Sludge blanket from alum with 800 mg/1 clay was more stable than the one from alum with 500 mg/1 of clay. Transition from lower to higher flow rates was very smooth with no visible disturbance to the blanket in the case of 800 mg/1 of clay, where as blanket with 500 mg/1 clay was mildly agitated during the transition. This indicates that sludge blanket clarifier, when operated at higher clay doses can more easily take the shock hydraulic loading.

EFFLUENT QUALITY

The overall physical and chemical parameters for colourless effluent obtained by treating waste with optimum alum and alum with clay have been incorporated in Table I. To ascertain the operational parameters of the model, colour, COD and SS removal were measured at different flow rates for three different treatments i. e. alum without any clay, alum with 500 mg/l clay and alum with 800 mg/l clay.

TABLE—I

CHARACTERISTICS OF UNTREATED AND TREATED WASTE WATER

Parameter	Unit	Untreated Waste Water	WASTE WATER TREATED WITH		
			Alum 500 mg/l	Alum 500 mg/l and clay 500 mg/l	Alum 500 mg/l and clay 800 mg/l
Total solids	mg/l	1410	1316-1746	1097-1306	1080-1267
+Suspended solids	mg/l	Negligible	295-654	39-65	32-42
pH	—	8.3	7.6	7.6	7.6
Alkalinity (Methyl orange)	mg/l	195	—	—	—
Acidity (CO_2)	mg/l	—	43	40	40
Sulphates	mg/l	300	454	454	454
++BOD_5	mg/l	550	435	435	435
COD	mg/l	1028	473-834	273-493	246-432
Colour	Co-Pt Unit	3500	170-180	75-100	70-105
Residual Alum (as Al_2O_3)	mg/l	—	4.5	4.5	4.5

Note :—

\+ Suspended solids of untreated waste are negligible, since settled waste water used throughout the investigation.

\+ + BOD_5 values are reported from jar test experiments conducted on the day sample was collected. All other parameters are for the range of flow rates in the clari-flocculator.

COLOUR REMOVAL

A high degree of colour removal was acheived in the laboratory flocculator. Residual colour of treated effluents at various flow rates have been given in Table II. For the waste of 3500 Co-Pt initial conc. colour removal of the order of 97-98% was achieved with alum and clay and 95% colour was removed when alum was used without any clay. Also jar tests carried out out on the same waste removed 94% of the colour. The increased removal of colour in upflow clariflocculator may possibly be due to absorption of significant amount of the dissolved colour by the sludge blanket (31). This hypothesis is further substantiated by the observation that in the initial stages of the flocculator operation, i. e. when the quantity of sludge accumulated was less, ths colour reduction was 94-95%, but increased with time as sludge started accumulating. The treated effluent was visibly clear and residual colour never increased beyond 105 Co-Pt units in the case of alum clay whereas the minimum residual colour with alum was 180 units.

REMOVAL OF SUSPENDED SOLIDS

Suspended solids escaping with the treated effluent and their percent removal at various flow rates in the sludge blanket clarifier for three different cases studied are given in Fig. 3. It is quite clear from these observations that SS in the effluent from alum-clay treatment is much less than the effluent from alum treatment. This is inspite of the initial SS in the waste water mixed with alum-clay being much more than waste water with alum alone. A maximum SS removal of 65% could be achieved at an equivalent rise rate of 7500 $l/m^2/day$ when only alum was used, whereas a removal of the order of 96 to 98% could be achieved at a rise rate of 32,000 $l/m^2/day$, when clay along with alum was used (Rise rate is around 4 times more than in the former case).

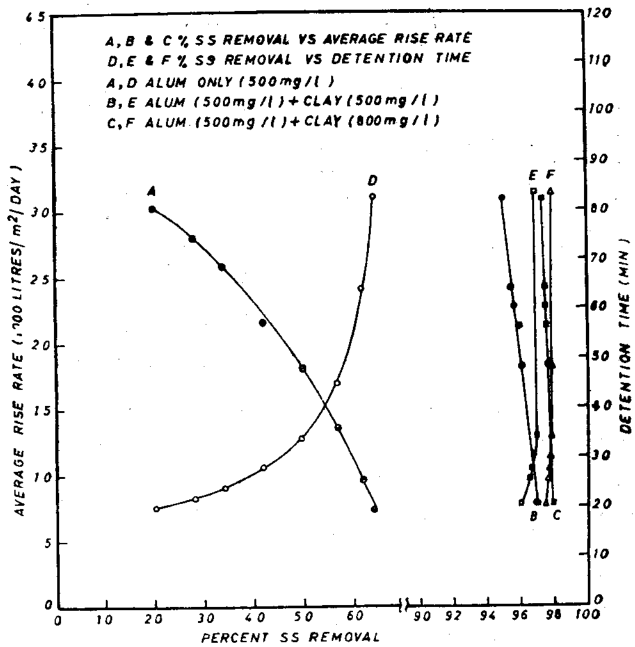

FIG 3. PERCENT SS REMOVAL AT VARIOUS RISE RATES AND DETENTION TIMES

TABLE—II
RESIDUAL COLOUR IN TREATED EFFLUENT AT VARIOUS FLOW RATES
INITIAL COLOUR CONCENTRATION = 3500 Co pt Units

Flow rate in the floeculator (LPM) (Figures in paranthesis-Equivalent average rise rates $l/m^2/day$)	COLOUR Co-pt UNITS		
	Alum only	Alum and 500 mg/l clay	Alum and 800 mg/l clay
0.65 (7300)	170	75	70
0.85 (9547)	175	—	—
1.20 (13478)	175	—	—
1.60 (17971)	170	80	80
1.80 (20217)	—	85	95
1.9 (21340)	—	—	—
2.00 (22464)	—	95	100
2.15 (24149)	—	100	100
2.30 (25833)	175	—	—
2.5 (28080)	175	—	—
2.7 (30326)	180	100	105

COD REDUCTION

COD of the waste water is contributed by both suspeded and dissolved organics. There are two possible modes viz. trapping of SS and absorption of dissolved organics by sludge blankets by which COD is reduced in the clariflocculator. The observations have been recorded in Fig. 4. As indicated, reduction in COD was found to be more when the waste water was treated with alum clay than with alum alone. This is largely due to the fact, that 96-98% of the SS have been retained in the sludge in the case of alum-clay treatment as against a maximum retention of 65% of SS with alum alone for the flow rates considered. Also, a significant part of the dissolved organics are possibly absorbed by the clay Laden sludge blanket. Reduction in COD was less at higher flow rates as compared to lower flow rates. It could be due to smaller contact times available for absorption at higher flow rates. It is evidenced by the fact that in the case of alum-clay SS removal is almost constant but COD removal varies with flow rate (Fig. 3, 4).

From these observations it is quite apparent that in the treatment of waste water with alum-clay, SS removal was not materially affected by decreasing the detention time from 83 min. to 20 min. The total solid, however, were increased by decreasing the detention time (Table III). It is due to the fact that dissolved organics do not get adsorbed at ϕ larger rise rate and eventually contribute to the total solids. In a trial run using alum and clay, flow was admitted at 4 LPM to the flocculator with corressponding detention time of 14 min. After the formation of blanket, SS and colour removal were comparable to those at longer detention periods.

Further, SVC_{30} tests conducted on flucculated mixed liquors indicated sludge volumes of 25 percent, 12 percent and 14 percent of the volumes of

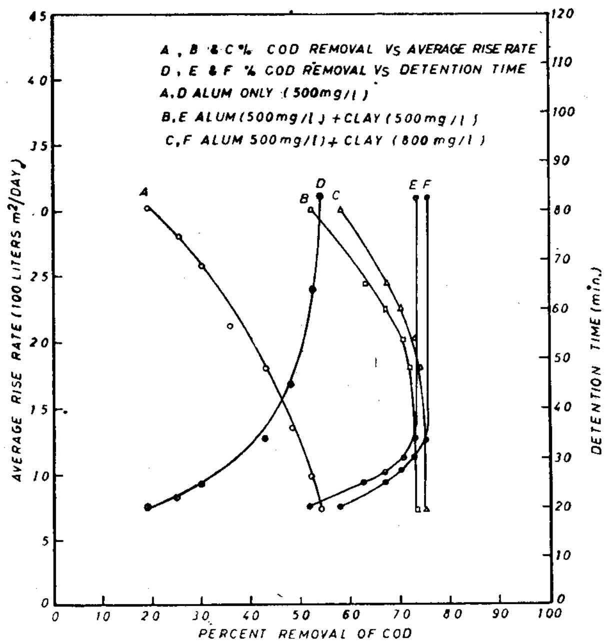

FIG. 4. PERCENT COD REMOVAT AT VARIOUS RISE RATES AND DETENTION TIMES

TABLE—III
TOTAL SOLIDS IN THE TREATED EFFLUENT

Flow Rate in the Flocculator (LPM) (Figures in paranthesis-Equivalent Average Rise Rates Litres/m²/day)	Alum 500 only (mg/l)	Alum 500 clay 500 (mg/l)	Alum 500 mg/l clay 500 (mg/l)
0.65 (7300)	1316	1097	1080
0.85 (9547)	1403	—	—
1.2 (13478)	1449	—	—
1.60 (17971)	1507	1125	1140
1.80 (20217)	—	1139	1106
1.90 (21340)	1596	—	—
2.00 (22464)	—	1187	1153
2.15 (24149)	—	1196	1147
2.30 (25833)	1608	—	—
2.50 (28080)	1600	—	—
2.70 (30326)	1746	1306	1267

the suspension for alum, alum with 500 mg/l clay and alum with 800 mg/l clay respcctively. But in the continuous operation of sludge blanket clarfier, sludges obtained represented 8-10 percent and 20-25 perecent of the total valume of the waste treated with and without clay respectively. Obviously, the sludge blanket gets compressed by overlying liquid in the clariflocculator. ([31]).

CONCLUSION

From the above results and discussion it obviously appears that clay assisted alum coagulation of the colouring matter can circumvent the problems encountered by massive lime treatment without additional cost of the treatment. The clarifier is a single unit in which floculation. settling, compaction filteration and absorption of soluble organics take place. This very single unit, when operated at low rise rates, is a complete treatment unit. Such an effluent can directly be discharged in receiving body. COD of the treated effluent is well within the limits prescribed by ISI code. However, before recommending such a process, it is necessary to carry out pilot plant studies. Also the possible disposal modes for 8-10 percent of the sludge of the total volume of the waste water treated should also be looked into. Work in this direction is in progress.

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